(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 March 2019 (14.03.2019)

WIPO | PCT

(10) International Publication Number
WO 2019/048693 A1

(51) International Patent Classification:
H01L 21/02 (2006.01) *H01L 21/311* (2006.01)

(21) International Application Number:
PCT/EP2018/074401

(22) International Filing Date:
11 September 2018 (11.09.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10 2017 120 963.8
11 September 2017 (11.09.2017) DE

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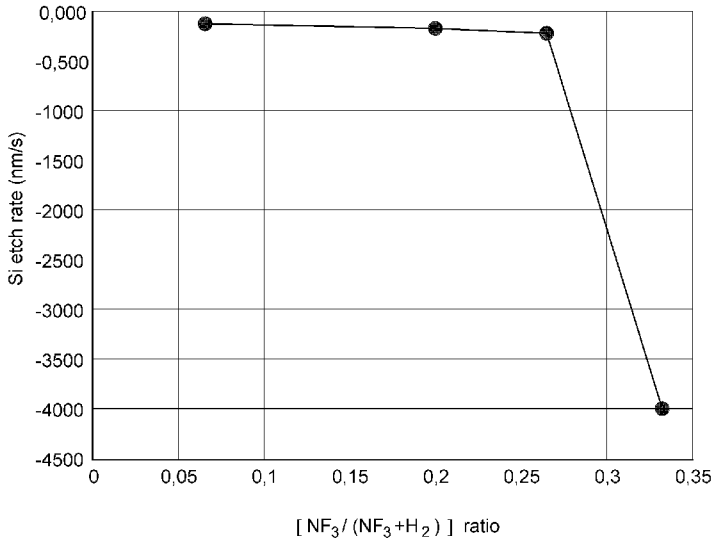
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME,

(54) Title: METHOD FOR ETCHING A SILICON CONTAINING SURFACE

Fig. 2



(57) Abstract: A Method for etching a silicon-containing surface of a substrate or a layer deposited on a substrate without forming solid adducts, wherein the method comprising: Flowing NF_3 and H_2 into an activation zone of a cleaning system or chamber, activating NF_3 and H_2 in the activation zone by forming H-radicals, forming gaseous HF in a first reaction of the H-radicals with NF_3 and reaction products of NF_3, flowing the gaseous HF to the surface and forming gaseous SiF_4 in a second reaction of HF with SiO_2 of the surface. The flow ratio of $R=(NF_3)/(NF_3+H_2)$ is less than 0.3 or is between 0.2 and 0.3. The substrate is maintained at a temperature between room temperature and 1050°C during the etching operation. The first reaction comprises first subsequent reactions of NF_2 with H-radicals and NF with H-radicals. The first reaction comprises second subsequent reactions forming

[Continued on next page]

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MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

NH_3. The first reaction comprises third subsequent reactions forming molecules comprising NH and F and F-radicals.

Description

Method for etching a silicon containing surface

Field of the Invention

[0001] The invention relates to a method of manufacturing thin films and coatings on a silicon-containing surface of a substrate or a layer grown on a substrate.

[0002] The method removes native oxides, as SiO_2 from the surface and leaves a smooth surface. The etching method forms a pre-process for a subsequent process for depositing a layer, in particular a III-V-layer on a clean, smooth surface of silicon.

State of the Art

[0003] US 8,501,629 B2 discloses a method of etching a silicon-containing layer by flowing a fluorine-containing precursor and a hydrogen-containing precursor into a remote plasma region. The hydrogen to fluorine atomic flow ratio is greater than 5:1. The state of the art prefers as fluorine containing precursor nitrogen tri-fluoride and as hydrogen-containing precursor ammonia. The method of the state of the art forms solid adducts, which have to be removed by sublimation at temperatures above 1000°C.

Summary of the Invention

[0004] It is an object of the invention to improve a dry etching method to avoid the additional sublimation step.

[0005] The method of the invention comprises the following steps:

Flowing NF_3 and H_2 into a plasma activation zone of a cleaning chamber,
activating NF_3 and H_2 in the plasma activation zone by forming H-radicals,
forming gaseous HF in a first reaction of the H-radicals with NF_3 and reaction products of NF_3,
flowing the gaseous HF to the surface and forming gaseous SiF_4 in a second reaction of HF with SiO_2 of the surface.

[0006] Optionally the method of the invention comprises additionally the following features:
the first reaction comprises first subsequent reactions of NF_2 with H-radicals and NF with H-radicals,
the first reaction comprises second subsequent reactions forming NH_4F and/or NH_3,
the first reaction comprises third subsequent reactions forming molecules comprising NH and F,
the flow ratio of $R=(NF_3)/(NF_3+H_2)$ is less than 0.3 and preferably is between 0.2 and 0.3,
the substrate is maintained at a temperature between room temperature and 1050°C during the etching operation, and a plasma is used for activating NF_3 and H_2.

[0007] In the activation zone a plasma decomposes at least molecular hydrogen into hydrogen radicals. NF_3 maybe decomposed in decomposition products as well. The activation zone is preferably located inside of a cleaning system or chamber. The plasma activation zone can be located outside of a vacuum chamber in which a process chamber is located wherein the substrate rests on a susceptor, which can be heated to elevated temperatures. A remote plasma source is connected with a showerhead via a conduit, which transports

the reactive radicals. The latter is located inside the vacuum chamber. The following overall reaction takes place in the activation zone:

$$NF_3 + 3H_2 \rightarrow 2HF + NH_4F \quad (1)$$

[0008] The following overall reaction takes place on the surface:

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O \quad (2)$$

[0009] NH_4F can decompose with the following reaction into NH_3:

$$NH_4F \rightarrow HF + NH_3 \quad (3)$$

[0010] HF is flown from the activation zone to a process zone of the cleaning chamber in an etching operation, wherein the substrate is located and kept at room temperature or at a temperature in a range between room temperature and 1050°C and especially below 30°C.

[0011] The gaseous HF reacts with solid SiO_2 to form gaseous SiF_4 and gaseous H_2O, which are removed by a carrier gas, which is flown into the process zone of the cleaning chamber as well. The carrier gas can be flown into the vacuum chamber by use of separate conduit. Preferable two separate conduits are connected to a gas inlet of a showerhead for flowing gas into the process chamber wherein the substrate rests on a heatable susceptor.

[0012] The cleaning system or chamber can be part of a clustered III-V epitaxial chamber, wherein in a growth chamber of a growth reactor a III-V-layer or a SiGeSn layer may be deposited on the pre-cleaned silicon containing layer, which may be the surface of a silicon wafer. The III-V-layer can be GaAs

or any other binary, ternary or quaternary compound based on Al, Ga, In as group-III elements and N, P, As, Sb as group-V elements.

[0013] The following subsequent reactions may occur:

	H_2	→	2H	(4)
	$H + NF_3$	→	$HF + NF_2$	(5)
	$H + NF_2$	→	HF + NF	(6)
	H + NF	→	HF + N	(7)
	H + N	→	NH	(8)
	H + NH	→	NH_2	(9)
	$H + NH_3$	→	NH_3	(10)
	$H + NF_3$	→	NHF_3	(11)
	NHF_3	→	$NHF_2 + F$	(12)
	NHF_2	→	NHF + F	(13)
	$H + NHF_2$	→	$NH_2F + F$	(14)
	$H + NHF_2$	→	HF + NHF	(15)
	H + NHF	→	HF + NH	(16)
	$H + NH_2F$	→	$HF + NH_2$	(17)

[0014] NH_4F, which is formed in (1) may decompose in reaction (3) into NH_3.

[0015] Reaction (4) shows the formation of H-radicals in the activation zone by the plasma. The reactions (5) to (7) are first subsequent reactions to form HF-molecules, which etch SiO_2 on the surface, but not the Si-atoms of the surface. Second subsequent reactions (8) and (10) form NH_3 in a reaction of nitrogen-containing reaction products with hydrogen atoms.

[0016] Reaction (11) shows a parallel reaction to reaction (5), wherein NF_3 reacts to NHF_3, which decomposes in third subsequent reactions (12) to (14) into fluorine atoms (F-radicals). The formation of fluorine atoms should be avoided as much as possible, since fluorine may destroy the silicon-containing surface. It is therefore proposed, that the gas ratio of NF_3 to the total precursor flow is less than 0.3.

[0017] Reactions (15) to (16) show a parallel reaction to reaction (13) of NHF_2, formed in reaction (12).

[0018] Reaction (16) shows a subsequent reaction to reaction (13).

[0019] Reaction (17) shows a subsequent reaction of reaction (14).

Brief description of the drawings

[0020] Figure 1 shows the different flows of $NF_3 + H_2$ keeping a constant total flow of 750 sccm, which was tested by flowing into the plasma activation zone.

[0021] Figure 2 shows the Si etch rate in function of $NF_3/(NF_3 + H_2)$ ratio, showing low Si-etch rate below 0.28 due to formation of HF-vapor (so a selective etch process to Silicon). Above 0.28 due to atomic F-formation the Si-etching is strongly enhanced.

[0022] Figures 3a shows SIMS profiles of the oxygen O-level measured in GaAs/Si hetero-structures with low bake temperature (650°C in the process growth chamber) on a pre cleaned substrate, at different NF_3/H_2 plasma etch time. In relation to this Figure 3b shows the (004) XRD FWHM at different NF_3/H_2 plasma etch time.

[0023] Figure 4 shows SIMS profiles of the O-level measured in GaAs/Si hetero structures with low bake temperature (650°C in the process growth chamber) showing the lower O-concentration at GaAs/Si interface by using in-situ NF_3/H_2 plasma compared to other ex-situ and in-situ etch treatments.

[0024] Figure 5 compares FWHM from (004) XRD scans of GaAs/Si hetero structure on a pre clean substrate after various ex-situ and in-situ etch treatments showing that similar crystal quality (i.e. low Full Width Half Maximum) can be obtained with low (650C) and high (950C) bake temperature by using in-situ NF_3/H_2 plasma preclean process at flow ratio <0.28.

[0025] Figure 6 shows schematic of a Cleaning system or chamber comprising gas inlet manifold, eventually heated susceptor, showerhead and vacuum pump; this is also equipped with Remote Plasma Source fed with NF_3, H_2 and/or Ar and additional separate carrier gases.

Detailed Description of the invention

[0026] A cluster process system unit comprises a growth chamber comprising a gas inlet device, a heated susceptor and a vacuum equipment. A pre-cleaned substrate comprising a silicon surface is transferred through a load lock into the growth chamber and is placed on the susceptor. The susceptor is heated to a process temperature. Volatile precursors comprising III- and V-elements are flown into the growth chamber. A III-V-layer is grown on the pre-cleaned substrate.

[0027] A cleaning system or chamber comprises a vessel, comprising a gas inlet device, an eventually heated susceptor, and a vacuum chamber which can be evacuated by means of a vacuum pump. Fig. 6 shows schematic of such a system or chamber equipped with Remote Plasma Source fed with NF_3, H_2 and/or Ar. The vessel is directly connected via the load lock with the growth chamber. In an alternative embodiment the growth chamber and the cleaning chamber are connected with a transfer chamber of a cluster process system, wherein the transfer chamber can be evacuated or flushed with an inert gas.

[0028] The cleaning system or chamber comprises an activation zone, especially a plasma activation zone, which is remote from an etching zone. The cleaning system comprises electrodes to create a plasma by high frequency such as radio frequency or Remote Plasma Source (RPS). NF_3 and H_2 are flown into the activation zone in a space between the electrodes. A noble gas (such as Ar) can be used as a carrier gas to dilute the precursors. The plasma activates the precursors to form gaseous HF and as less as possible fluorine atoms. The reaction products of the reactions in the plasma zone are flown into the etching zone, in which a substrate is located on a support. In the embodiment the temperature of the substrate is room temperature. HF reacts with SiO_2 on the

surface of the substrate to form SiF_4 and H_2O. The total pressure in the cleaning system is far below atmospheric pressure: at these conditions SiF_4 and H_2O are vapors. Gaseous SiF_4 and gaseous H_2O are removed by the carrier gas out of the etching zone.

[0029] The pressure conditions are kept at 1 Torr to obtain a clean O-free Si surface.

[0030] Figure 2 shows that the Si etch rate increases dramatically at ratios over 0.28 due to an increased atomic F generation. At lower ratios the etch rate of silicon is nearly constant at a low level due to HF-vapor generation.

[0031] After cleaning the surface from the oxide, the substrate is carried through the load lock directly into the process chamber to grow the III-V-layer on top of the surface.

[0032] To remove oxygen, which possibly adsorb on the silicon surface, the substrate can be baked, prior to the growth of the III-V-layer, at an elevated temperature in particular at 650°C (which is close to the III-V layer growth). This may be processed in the process growth chamber of the cluster.

[0033] Figure 3a and 3b show a good agreement between XRD- and SIMS-analysis. It shows the crystal quality degradation with residual native oxide after in situ NF_3/H_2 plasma process. The 30 seconds´ process shows lower O contamination at the interface and lower XRD FWHM.

[0034] The cleaning system or chamber shown in figure 6 comprises a vacuum chamber 1 having an inlet 2 for flowing process gases into a process chamber located in the vacuum chamber 1. Two separate conduits 2′, 2′′ are connected

with the gas inlet 2 through which gas flows from outside of the vacuum chamber 1 into the vacuum chamber 1.

[0035] A gas inlet manifold 4 comprises a H_2-Source, an Ar-Source and an NF_3-Source. A remote Plasma Source 3 is located between the gas inlet manifold 4 and a showerhead 5 which is located inside the vacuum chamber 1 to flow the process gases into process chamber. The gas conduit 2′ connects the plasma source 3 with the gas inlet 2. A separate carrier gas source 9 is able to flow Argon or Hydrogen through a conduit 2′′ into the gas inlet 2.

[0036] A Susceptor 7 forms the bottom of the process chamber. A substrate 6 is located on a surface of the Susceptor 7 which faces a gas outlet surface of the showerhead 5. The susceptor 7 comprises heating elements to heat the substrate 6.

[0037] A gas outlet 8 is connected with a vacuum pump to evacuate the vacuum chamber 1.

[0038] All disclosed features are essential to the invention (taken in isolation, but also in combination with each other). The disclosure of the application hereby also includes the disclosure content of the accompanying/attached priority documents (copy of preliminary application) in its entirety, also for the purpose of also incorporating features of these documents into the claims of the present application. The features in the subclaims characterize independent inventive further developments of prior art, in particular so as to generate partial applications based upon these claims.

Claims

1. Method for etching a silicon-containing surface of a substrate or a layer deposited on a substrate without forming solid adducts, wherein the method comprising:

Flowing NF_3 and H_2 into an activation zone of a cleaning system or chamber,

activating NF_3 and H_2 in the activation zone by forming H-radicals,

forming gaseous HF in a first reaction of the H-radicals with NF_3 and reaction products of NF_3,

flowing the gaseous HF to the surface and forming gaseous SiF_4 in a second reaction of HF with SiO_2 of the surface, characterized in that the ratio of the mass flows $R=(NF_3)/(NF_3+H_2)$ is lower than 0,3 and in that the substrate is maintained at a temperature between room temperature and 1050°C during the second reaction.

2. Method of claim 1, wherein the flow ratio of $R=(NF_3)/(NF_3+H_2)$ is between 0.2 and 0.3.

3. Method of claim 1, wherein the flow ratio of $R=(NF_3)/(NF_3+H_2)$ is between 0.2 and 0.28.

4. Method of any of claims 1 to 3, wherein the first reaction comprises second subsequent reactions forming NH_3.

5. Method of any of claims 1 to 4, wherein the first reaction comprises third subsequent reactions forming molecules comprising NH and F and F-radicals.

6. The method of any of claims 1 to 5, wherein the substrate is maintained at a temperature between room temperature to 650°C during the etching operation.

7. The method of any of claims 1 to 6, wherein the substrate is maintained at a temperature below 30°C during the etching operation.

8. The method of any of claims 1 to 7, wherein activating NF_3 and H_2 is performed in a plasma or other activating sources.

Fig: 1

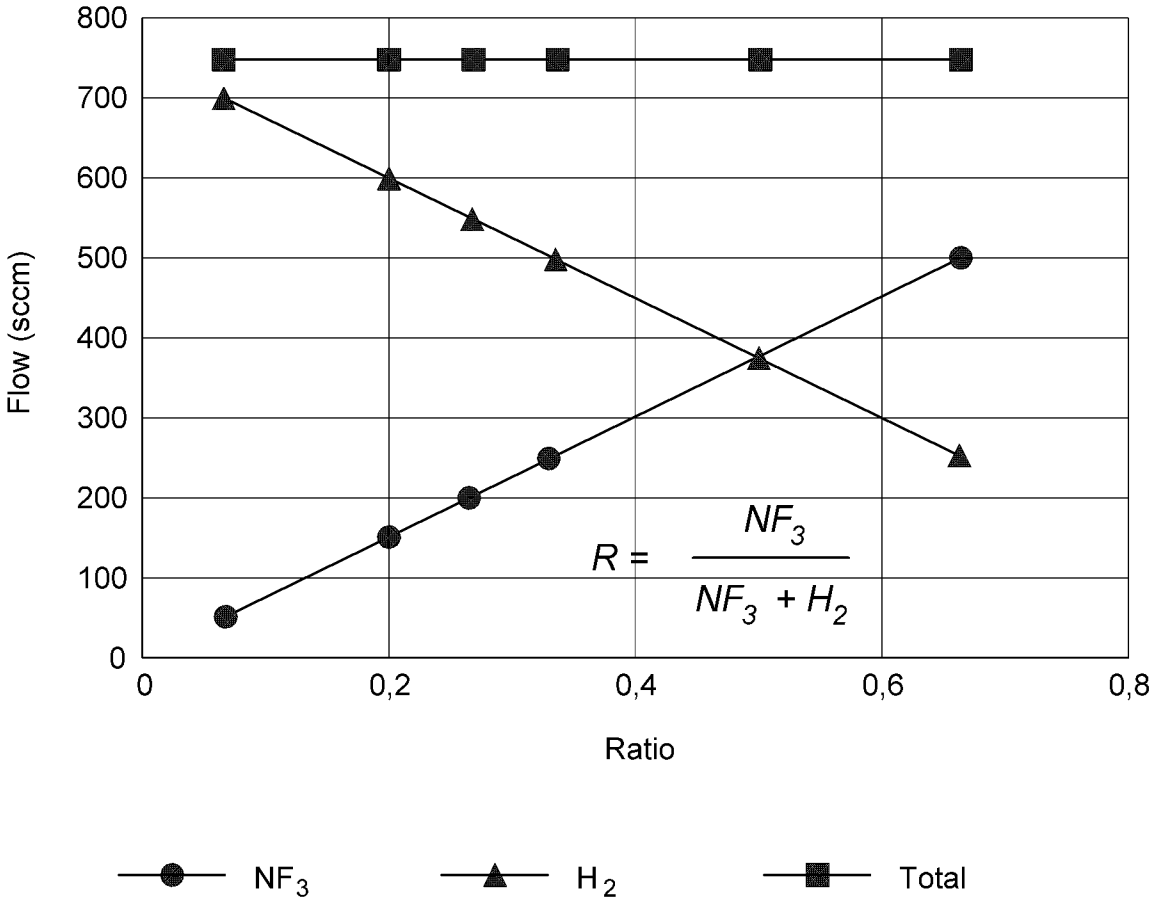

800
700
600
500
400
300
200
100
0
Flow (sccm)
0
0,2
0,4
0,6
0,8
Ratio
R = NF3 / (NF3 + H2)
NF3
H2
Total

Fig: 2

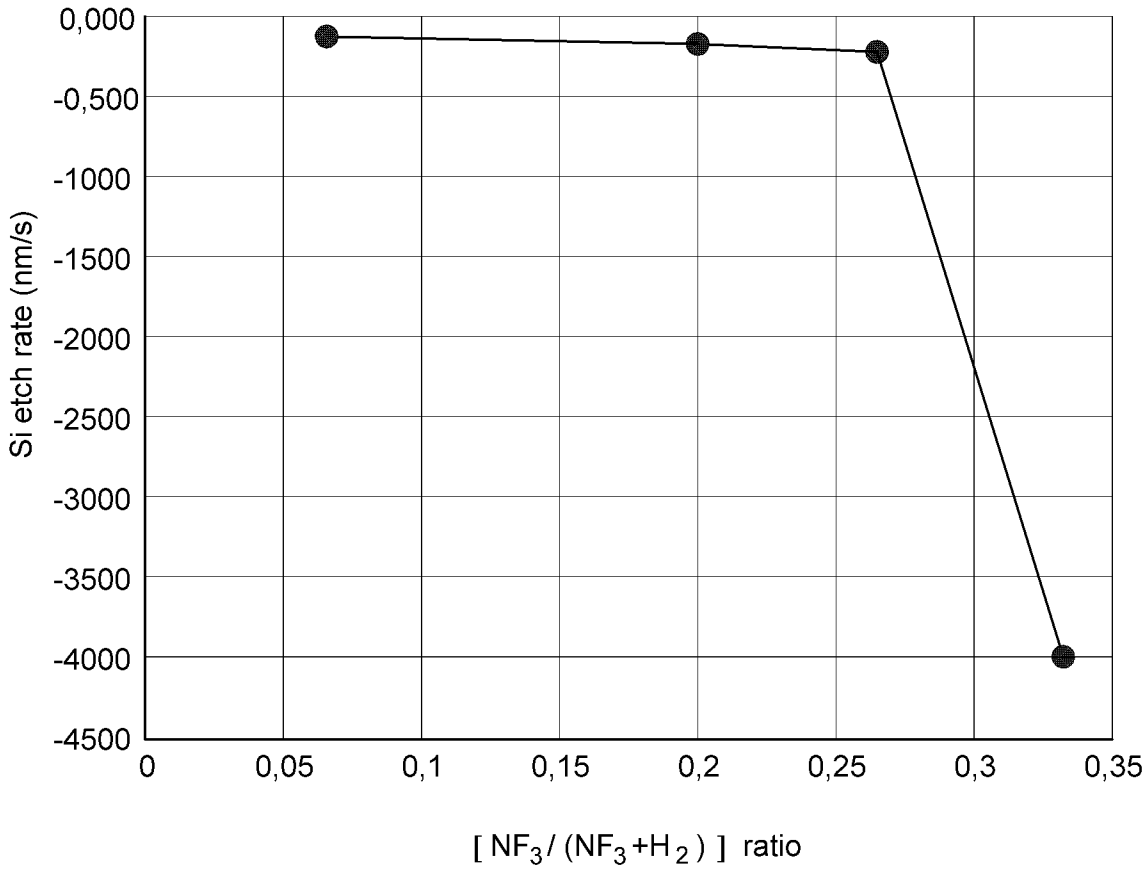

0,000
-0,500
-1000
-1500
-2000
-2500
-3000
-3500
-4000
-4500
Si etch rate (nm/s)
0
0,05
0,1
0,15
0,2
0,25
0,3
0,35
[NF3 / (NF3 +H2)] ratio

Fig: 3a

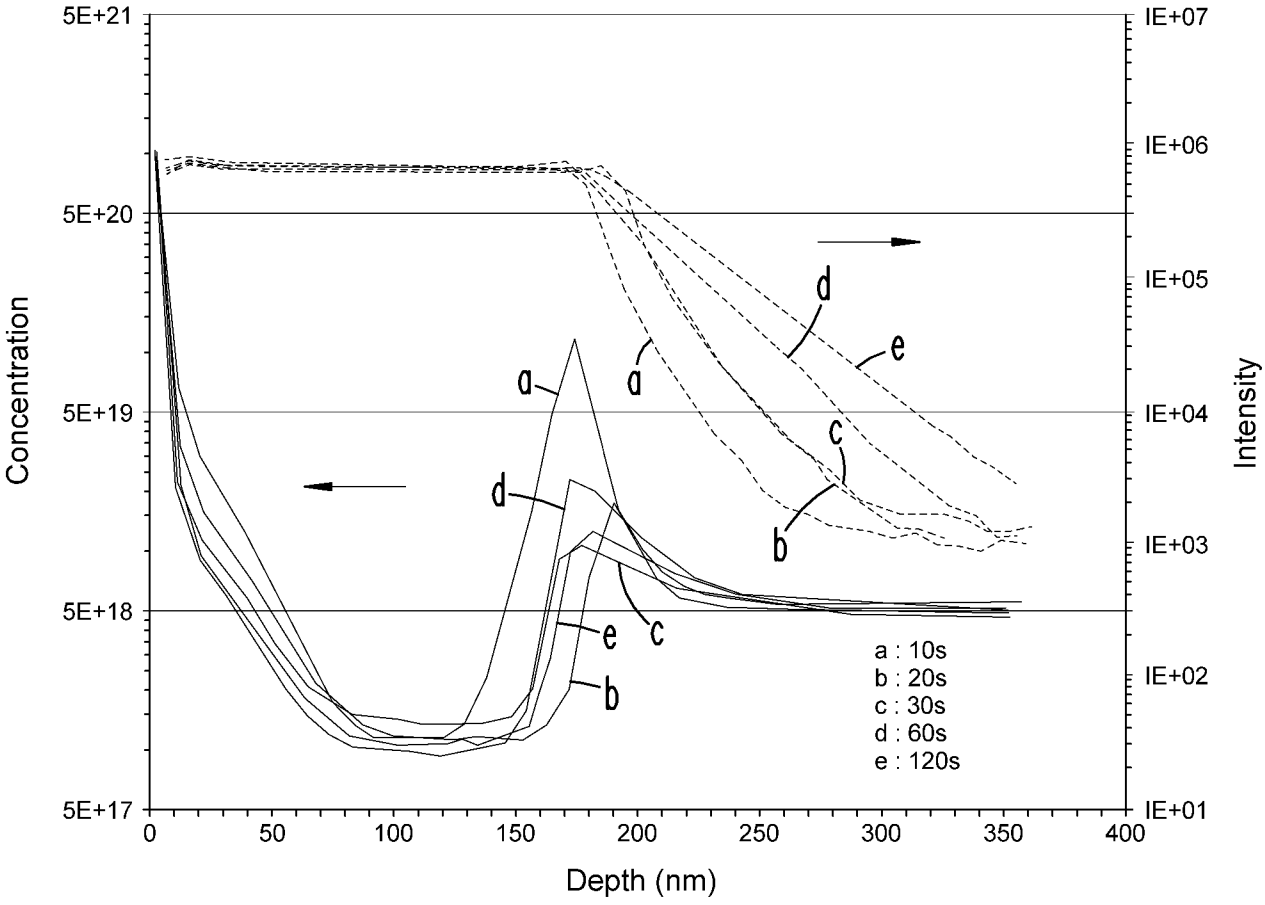

5E+21
5E+20
5E+19
5E+18
5E+17
IE+07
IE+06
IE+05
IE+04
IE+03
IE+02
IE+01
Concentration
Intensity
Depth (nm)
0
50
100
150
200
250
300
350
400
a : 10s
b : 20s
c : 30s
d : 60s
e : 120s

Fig: 3b

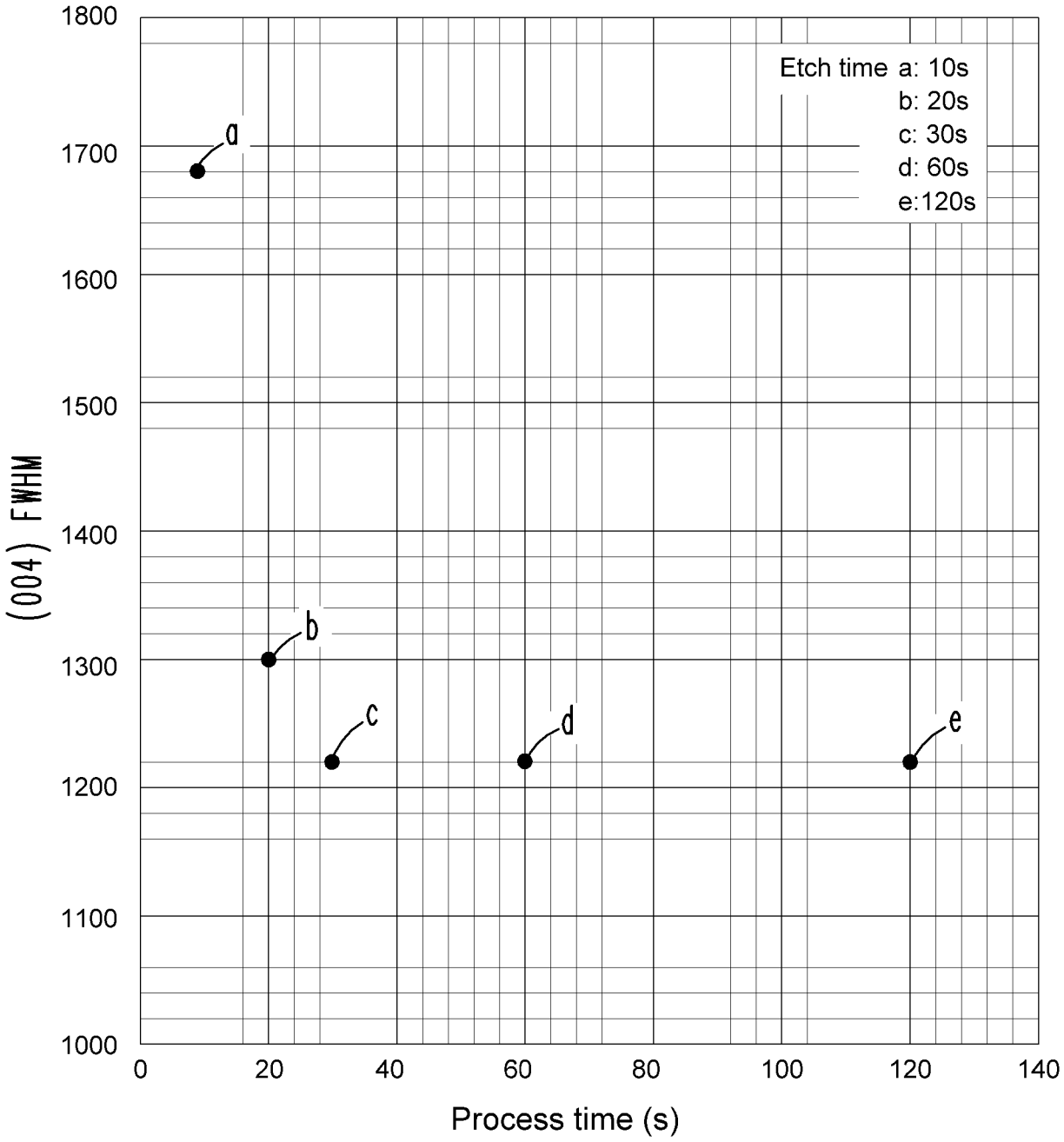

1800
1700
1600
1500
1400
1300
1200
1100
1000
(004) FWHM
0
20
40
60
80
100
120
140
Process time (s)
Etch time a: 10s
b: 20s
c: 30s
d: 60s
e:120s
a
b
c
d
e

Fig: 4

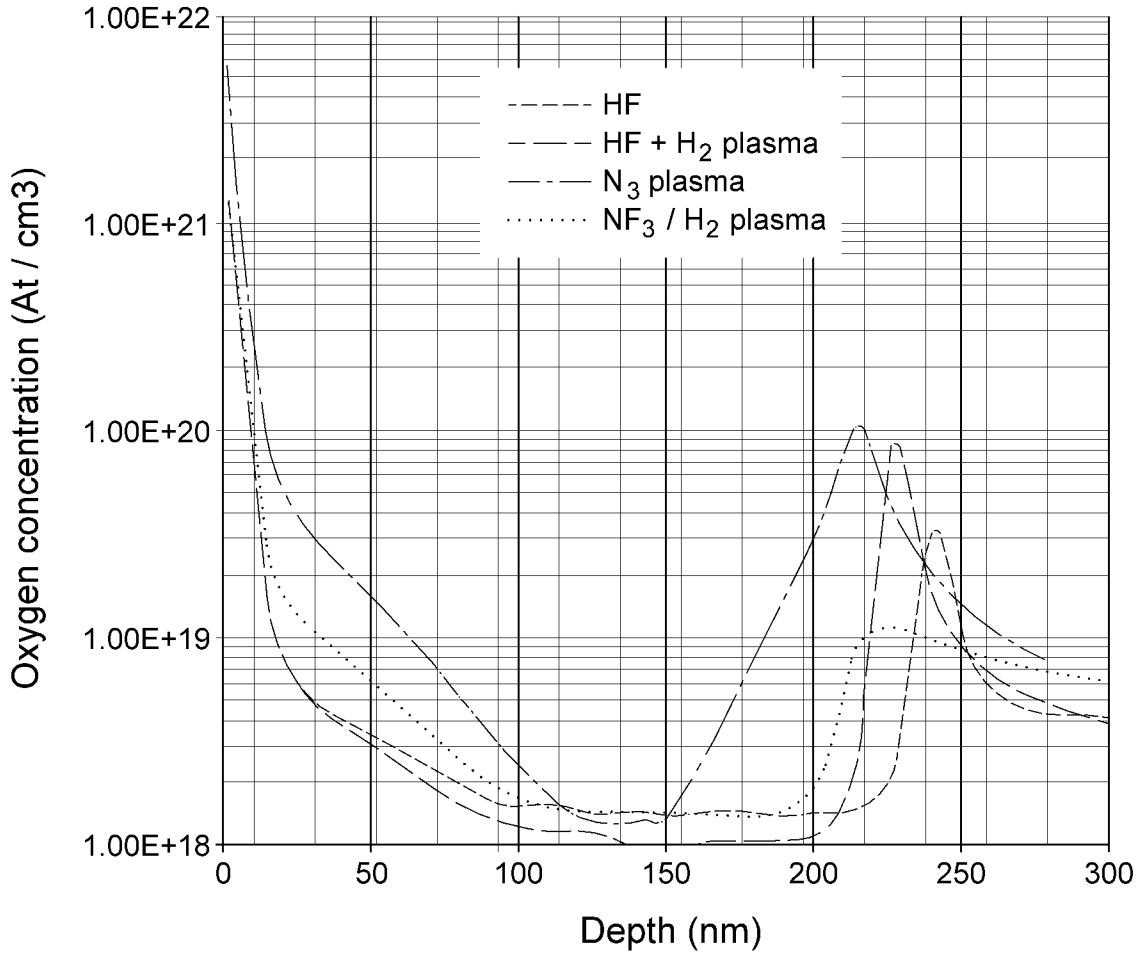
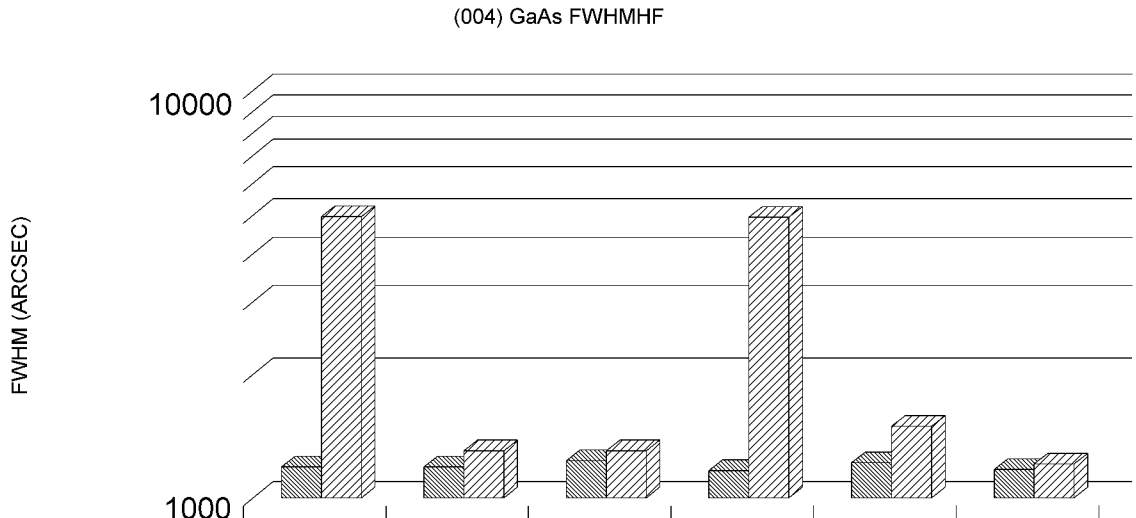
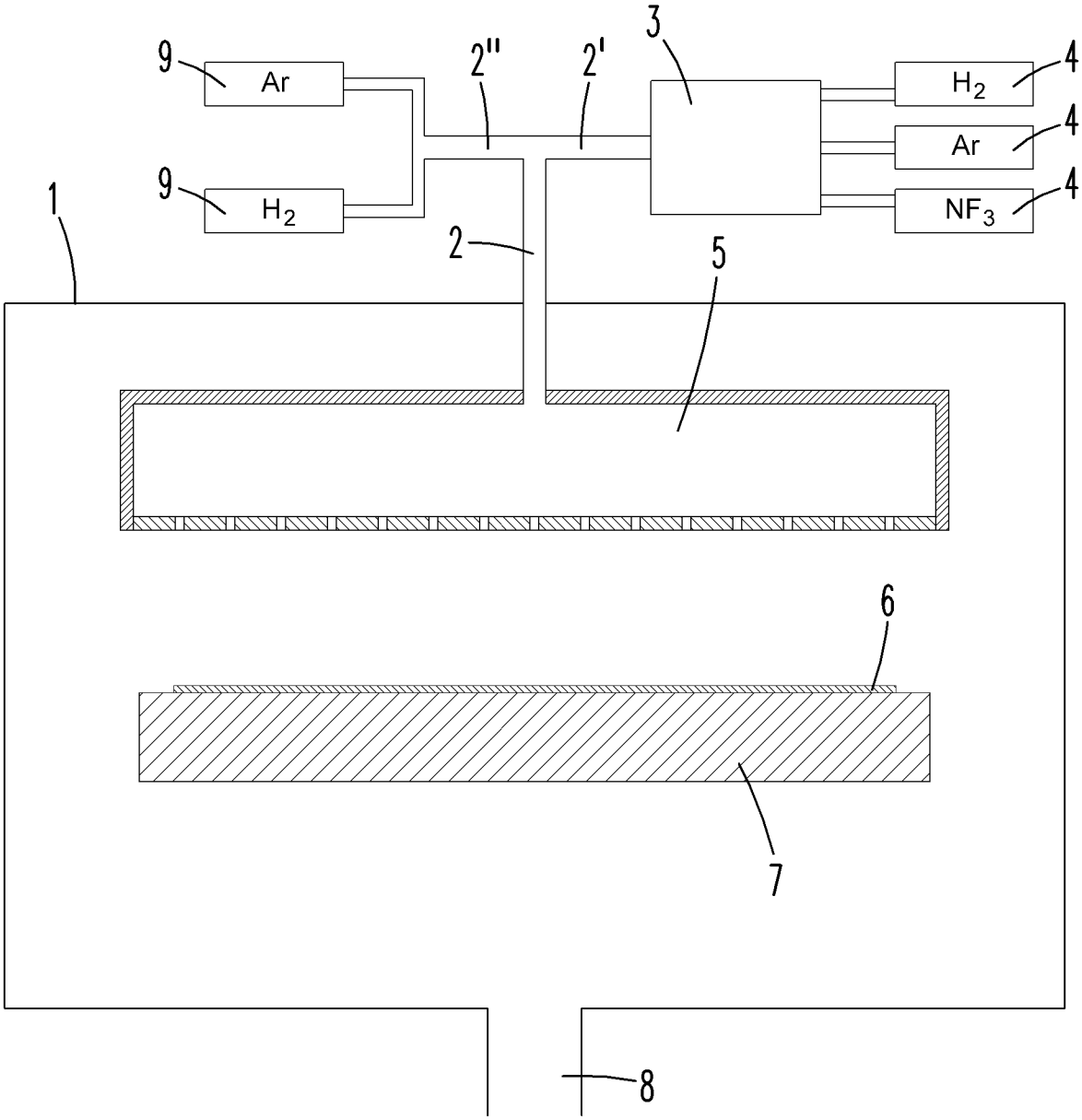

1.00E+22
1.00E+21
1.00E+20
1.00E+19
1.00E+18
Oxygen concentration (At / cm3)
0
50
100
150
200
250
300
Depth (nm)
HF
HF + H2 plasma
N3 plasma
NF3 / H2 plasma

Fig:5



	N/A	HF (wert.)	HF (wert.) +H_2 plasma	H_2 plasma	NF_3 plasma	NF_3/H_2 plasma
FWHM (HT bake)	1199	1182,5	1233,9	1164,3	1218,8	1195
FWHM (LT bake)	5000	1309,8	1302,3	5000	1487,7	1220

Fig: 6



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/074401

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L21/02 H01L21/311
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/104782 A1 (LU XINLAING [US] ET AL) 23 April 2009 (2009-04-23) paragraphs [0029] - [0046]; figures 3A,3B ----- -/--	1-8

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 December 2018	12/12/2018

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Szarowski, Anne

2

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FRYSTAK D C ET AL: "Pre-oxidation cleaning of silicon using remote plasma", PROCEEDINGS OF THE SECOND INTERNATIONAL SYMPOSIUM ON CLEANING TECHNOLOGY IN SEMICONDUCTOR DEVICE MANUFACTURING : [HELD AT THE ELECTROCHEMICAL SOCIETY FALL MEETING IN PHOENIX, ARIZONA, OCTOBER 14 - 18, 1992 (I.E. 1991!)] / ED. BY JERZY RUZYLLO, PENNIN, 14 October 1992 (1992-10-14), pages 58-71, XP009509772, ISBN: 978-1-56677-012-5 abstract Experimental; figure 1 C. Oxide Etching; figure 7 -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2018/074401

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009104782 A1	23-04-2009	CN 102160154 A	17-08-2011
		JP 2012505530 A	01-03-2012
		KR 20110084419 A	22-07-2011
		TW 201025446 A	01-07-2010
		US 2009104782 A1	23-04-2009
		WO 2010042552 A2	15-04-2010